(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 December 2003 (24.12.2003)

PCT

(10) International Publication Number
WO 03/106375 A1

(51) International Patent Classification[7]: C04B 40/00, 28/02, 22/12 // 103:10, 111:10

(21) International Application Number: PCT/EP03/05456

(22) International Filing Date: 22 May 2003 (22.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0213765.1 17 June 2002 (17.06.2002) GB
0304158.9 25 February 2003 (25.02.2003) GB

(71) Applicant *(for all designated States except US)*: CONSTRUCTION RESEARCH & TECHNOLOGY GMBH [DE/DE]; Dr. Albert-Frank-Str. 32, 83308 Trostberg (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: ANGELSKAAR, Terje [NO/CH]; Honeretshof 6, CH-8962 Bergdietikon (CH). IWATA, Raita [JP/JP]; 305 Shounannryou, 2722 Hagizono, Chigasaki, Kanagawa 2722 (JP).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 03/106375 A1

(54) Title: ACCELERATOR ADMIXTURE

(57) Abstract: An accelerator composition for use with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3 Component 1 - aluminium sulphate Component 2 - at least one of an alkanolamine and an alkylene diamine or triamine Component 3 - hydrofluoric acid optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present: Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate; Component 5 - $C_1$- $C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts; Component 6 - aluminium hydroxide; Component 7 - at least one of phosphoric acid and phosphorous acid. The accelerators have excellent long-term stability and work well with "difficult" cements, such as some Japanese OPCs.

10/516699
DT15 Rec'd PCT/PTO 02 DEC 2004
PCT/EP03/05456

# ACCELERATOR ADMIXTURE

This invention relates to low alkali and alkali-free accelerators for sprayed cementitious compositions.

The use in cementitious compositions such as concrete to be applied by spraying of low alkali and alkali-free accelerators in place of the traditional aluminates and other strongly alkaline materials is now well established. The major components of such accelerators are aluminium compounds, the most commonly encountered being aluminium sulphate and amorphous aluminium hydroxide. In addition to these aluminium compounds, a variety of other components have been used in such accelerators, these including alkanolamines, other aluminium salts (such as oxalates and nitrates) and various organic acids. More recent compositions have involved the use of fluoride ions.

The major problem in the art is to find an accelerator composition that combines acceptable performance, acceptable stability and an acceptable compressive strength. Stability can be a problem, especially in the more extreme conditions sometimes encountered in tunnels, and a reasonable shelf-life is necessary for a practical accelerator. All accelerators used in spraying concrete lower the compressive strength compared to the compressive strength of the same concrete without accelerator. It is necessary that this lowering be kept to a minimum. In addition, a good early strength development in the 1-4 hour period after spraying is particularly desired.

In addition, the worldwide variation in cement types causes problems. What works well with one cement in, say, Europe will not necessarily work so well with an Australian or a Japanese cement. It is difficult to formulate an accelerator that will work acceptably well with all types.

It has now been found that a particular combination of materials gives an accelerator that performs especially well and is very stable. The invention therefore provides an accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate
Component 2 – at least one of an alkanolamine and an alkylene diamine or triamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present;

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;
Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - aluminium hydroxide;
Component 7 - at least one of phosphoric acid and phosphorous acid

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;
Component 2 - from 0.1 to 15%
Component 3 - from 0.2 to 8.0%
Component 4 - up to 15%
Component 5 - up to 15%
Component 6 - up to 15%
Component 7 - up to 5%.

Component 1, aluminium sulphate, may be any aluminium sulphate used in the manufacture of accelerators. It may be fully hydrated, or totally or partially calcined. A typical grade, and the one on which the proportion is based, is "17%" aluminium sulphate ($Al_2(SO_4)_3.14.3H_2O$) (called thus because that is the proportion of aluminium oxide therein). should any other aluminium sulphate be required, he appropriate quantity can be easily calculated on this basis. Preferably Component 1 is present in the proportion of from 30-46% by weight of the total accelerator composition.

Component 2, alkanolamine, alkylene diamine and alkylene triamine may be any such material, but is preferably ethylene diamine, ethylene triamine, diethanolamine or triethanolamine, most preferably diethanolamine. It is preferably present in the proportion of from 0.1- 10%, more preferably from 0.1 –8%, by weight of the total accelerator composition. It is possible to use a combination of two or more of such materials.

Component 3, hydrofluoric acid is generally used as an aqueous solution of about 40% HF by weight. The proportion of hydrofluoric acid present in the total accelerator composition (as HF) is preferably from 2-6%, more preferably from 2-4%, by weight of the total accelerator.

Component 4 may be selected from among the materials previously named. Although sodium and potassium are alkali metals, the proportion of such metals in the accelerator compositions according to this invention may be sufficiently low to permit these accelerators to be considered as alkali-free according to the accepted European definition (lower than 1% (weight) of $Na_2O$ equivalent). Up to 8.5% $Na_2O$ equivalent is considered "low alkali" and is acceptable for many purposes – in many cases, rigorous exclusion of alkali on health and environmental grounds is not necessary and a small proportion of at least one alkali metal enhances the early strength development. Thus, for the purposes of this invention, and contrary to the current practices of the art with respect to alkali-free accelerators, it is preferred that a minor proportion of alkali metal be present. This proportion is preferably no higher than 5% $Na_2O$ equivalent. The preferred proportion of Component 4 is from 1-10% by weight of the total accelerator composition. Component 4 is typically added to the accelerator composition as a 30% weight solution in water.

Component 5 may be selected from one or more of the group of acids. Especially preferred are formic, oxalic and glycolic acids and their metal salts, but other acids, such as acetic, propionic, succinic, citric and tartaric acids are also useful. Preferred proportions of Component 5 are from 2 - 10%, more preferably from 4 - 8%, by weight of the total accelerator composition.

It is required that at least one of Component 4 and Component 5 be present in the composition. The preferred Components 4 and/or 5 for the purposes of this invention are sodium oxalate, potassium oxalate and mixtures of one or both of these with lithium hydroxide. The LiOH/sodium-potassium oxalate mixtures are particularly preferred.

Component 6, aluminium hydroxide, is preferably amorphous aluminium hydroxide of the type normally used in accelerators for sprayed concrete. It is preferably present in the proportion of up to 10% by weight of the total accelerator composition. It is possible to use crystalline aluminium hydroxide; this is considerably cheaper, but it is difficult to dissolve and it does not perform as well as the amorphous material.

Component 7, phosphoric acid ($H_3PO_4$) or phosphorous acid ($H_3PO_3$), acts as a stabiliser. Although it is possible to omit it, it confers a useful degree of stability on the accelerator compositions of this invention, a vital consideration in tunnelling operations where the accelerator may have to remain in a ready-to-use state for long periods. It is therefore preferably present, and in a concentration of from 0.1- 2% by weight of the accelerator composition. It is possible to use a blend of both acids, but it is preferred to use phosphoric acid alone.

The accelerator compositions may be prepared by simply mixing the abovementioned components in any order and stirring to give an aqueous solution. In some cases, additional water will need to be added. The final composition will generally comprise from 40-70% by weight of water.

Given the nature of the ingredients, the resulting accelerator composition will not be a simple mixture of ingredients but a complex blend of reaction products. For example, the HF will react with some other components (most especially aluminium hydroxide, if any be present). This composition is very stable, having a shelf life under normal storage conditions of several months.

In use, the accelerator composition of the invention is injected at a spray nozzle in the conventional manner. The dose is typically from 5 – 12% by weight accelerator composition

based on cement weight. The invention also provides a method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator as hereinabove described.

Sprayed cementitious compositions that utilise accelerator compositions according to this invention exhibit an unusually rapid build-up of compressive strength. In addition, the accelerator compositions work well with an unusually wide variety of cements, including Japanese cements, with which other alkali-free accelerators give less satisfactory results. The invention also provides a hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator as hereinabove described.

The invention is further illustrated by the following non-limiting examples in which all parts are by weight.

A number of accelerators are added to a test mortar mix having the following constitution:

| | |
|---|---|
| water | 198 parts |
| ordinary Portland cement | 450 " |
| sand (DIN 196-1) | 1350 " |
| superplasticiser | 2.7 " |

The cement is Tayheiyo OPC, a commonly-used Japanese cement. The superplasticiser used is NT-1000 ex NMB Ltd., Japan.

Example 1

To the abovementioned mix is added with thorough mixing 31.5 parts of an accelerator according to the invention and having the following composition (given as percentages by weight):

| | |
|---|---|
| aluminium sulphate ($16H_2O$) | 35 |
| diethanolamine | 2.1 |
| sodium sulphate | 11.2 |
| oxalic acid | 7.5 |
| hydrofluoric acid | 6 |
| amorphous aluminium hydroxide | 9.5 |
| water | to 100% |

Example 2

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA162.

Example 3

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA170.

The samples are tested for compressive strength according to prEN (preliminary European Standard) 12394 and the results obtained are shown below:

| Example No. | Compressive strength (MPa) at | | |
|---|---|---|---|
| | 6h | 1d | 7d |
| 1 | 3.6 | 20.1 | 39 |
| 2 | 1.4 | 1.8 | 23.2 |
| 3 | 0.8 | 8.6 | 28.9 |

It can be seen that the composition comprising the accelerator according to the invention develops compressive strength earlier than the compositions comprising the commercial accelerators, and that the final strength is substantially higher.

CLAIMS:

1. An accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate
Component 2- at least one of an alkanolamine and an alkylene diamine or triamine
Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;
Component 5 - $C_1 - C_{10}$ aliphatic mono- and dicarboxylic acids and their metal salts;
Component 6 - aluminium hydroxide;
Component 7 - at least one of phosphoric acid and phosphorous acid.

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;
Component 2 - from 0.1 to 15%
Component 3 - from 0.2 to 8.0%
Component 4 - up to 15%
Component 5 - up to 15%
Component 6 - up to 15%
Component 7 - up to 5%.

2. An accelerator according to claim 1, in which Component 4 is present.

3. An accelerator according to claim 2, in which Component 4 contains alkali metal to the extent of from 1-8.5% $Na_2O$ equivalent.

4. An accelerator according to claim 3, in which the alkali metal equivalent is 5% $Na_2O$ equivalent maximum.

5. A method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator according to claim 1.

6. A hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator according to claim 1.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/05456

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B40/00 C04B28/02 C04B22/12 //C04B103:10,C04B111:10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 1 167 317 A (SIKA AG)<br>2 January 2002 (2002-01-02)<br>paragraphs '0004!-'0040!<br>example 1 | 1-6 |
| Y | --- | 2-4 |
| Y | PATENT ABSTRACTS OF JAPAN<br>vol. 1999, no. 03,<br>31 March 1999 (1999-03-31)<br>& JP 10 330139 A (CHICHIBU ONODA CEMENT CORP;ONODA CO),<br>15 December 1998 (1998-12-15)<br>abstract<br>paragraphs '0001!-'0018!<br>tables 2-4 | 2-4 |
| | --- | |
| | -/-- | |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 26 August 2003 | 09/09/2003 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Gattinger, I |

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/05456

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | PATENT ABSTRACTS OF JAPAN<br>vol. 1999, no. 04,<br>30 April 1999 (1999-04-30)<br>& JP 11 021158 A (CHICHIBU ONODA CEMENT CORP;ONODA CO; OHBAYASHI CORP),<br>26 January 1999 (1999-01-26)<br>abstract<br>paragraphs '0001!-'0013!<br>table 4 | 2-4 |
| A | EP 1 167 315 A (SIKA AG)<br>2 January 2002 (2002-01-02)<br>paragraphs '0004!-'0041!<br>example 1 | 1,5,6 |
| A | WO 01 42165 A (HOFMANN THOMAS ;MBT HOLDING AG (CH)) 14 June 2001 (2001-06-14)<br>page 1, line 21 -page 3, line 22<br>examples 1-5 | 1,5,6 |
| A | WO 98 18740 A (LUNKENHEIMER RUDOLF ;SEDELIES REINHOLD (DE); ALTMANN HORST (DE); B) 7 May 1998 (1998-05-07)<br>page 2, line 11 -page 3, line 29 | 2-4 |
| A | EP 0 657 398 A (SIKA AG)<br>14 June 1995 (1995-06-14)<br>page 2, line 14 -page 7, line 35<br>example 10 | |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/05456

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 1167317 A | 02-01-2002 | EP 1167317 A1 | 02-01-2002 |
| | | AU 5188301 A | 03-01-2002 |
| | | CA 2349796 A1 | 21-12-2001 |
| | | JP 2002080250 A | 19-03-2002 |
| | | NZ 512250 A | 26-11-2002 |
| | | US 2002035952 A1 | 28-03-2002 |
| JP 10330139 A | 15-12-1998 | NONE | |
| JP 11021158 A | 26-01-1999 | NONE | |
| EP 1167315 A | 02-01-2002 | EP 1167315 A1 | 02-01-2002 |
| | | AU 5188201 A | 03-01-2002 |
| | | CA 2349997 A1 | 21-12-2001 |
| | | JP 2002029801 A | 29-01-2002 |
| | | NZ 512249 A | 26-11-2002 |
| | | US 2002023574 A1 | 28-02-2002 |
| WO 0142165 A | 14-06-2001 | AT 240913 T | 15-06-2003 |
| | | AU 2671901 A | 18-06-2001 |
| | | BR 0016261 A | 20-08-2002 |
| | | CA 2393458 A1 | 14-06-2001 |
| | | CN 1407954 T | 02-04-2003 |
| | | DE 60002918 D1 | 26-06-2003 |
| | | WO 0142165 A2 | 14-06-2001 |
| | | EP 1237827 A2 | 11-09-2002 |
| | | HU 0204379 A2 | 28-06-2003 |
| | | JP 2003516303 T | 13-05-2003 |
| | | NO 20022662 A | 08-08-2002 |
| | | NZ 519441 A | 30-05-2003 |
| | | SK 9772002 A3 | 04-03-2003 |
| | | US 2002195026 A1 | 26-12-2002 |
| WO 9818740 A | 07-05-1998 | WO 9818740 A1 | 07-05-1998 |
| | | AT 196453 T | 15-10-2000 |
| | | CA 2271629 C | 25-03-2003 |
| | | CZ 9901399 A3 | 17-11-1999 |
| | | DE 59605932 D1 | 26-10-2000 |
| | | DK 946451 T3 | 13-11-2000 |
| | | EP 0946451 A1 | 06-10-1999 |
| | | FI 990920 A | 23-04-1999 |
| | | GR 3035038 T3 | 30-03-2001 |
| | | JP 2001509124 T | 10-07-2001 |
| | | KR 2000052720 A | 25-08-2000 |
| | | NO 991769 A | 14-04-1999 |
| | | PL 332831 A1 | 11-10-1999 |
| | | SK 51599 A3 | 10-12-1999 |
| | | US 6302954 B1 | 16-10-2001 |
| EP 0657398 A | 14-06-1995 | CH 686513 A5 | 15-04-1996 |
| | | AT 153010 T | 15-05-1997 |
| | | CA 2137309 A1 | 07-06-1995 |
| | | DE 69403183 D1 | 19-06-1997 |
| | | DE 69403183 T2 | 09-10-1997 |
| | | DK 657398 T3 | 15-12-1997 |
| | | EP 0657398 A1 | 14-06-1995 |
| | | ES 2102757 T3 | 01-08-1997 |
| | | GR 3024213 T3 | 31-10-1997 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/05456

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0657398 A | | JP 2930529 B2 | 03-08-1999 |
| | | JP 8048553 A | 20-02-1996 |
| | | NO 944681 A | 07-06-1995 |
| | | US 5560774 A | 01-10-1996 |